

# On optical spectroscopy of molecular junctions

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## Abstract

We compare theoretical techniques utilized for description of optical response in molecular junctions, and their application to simulate Raman spectroscopy in such systems. Strong and weak sides of the Hilbert vs. Liouville space, as well as quasiparticles vs. many-body states, formulations are discussed. Common origins of the methodologies and different approximations utilized in different formulations are identified.

## I. INTRODUCTION

The interaction of light with molecules is an important field of research due to its ability to provide information on molecular structure and dynamics, and to serve as a control tool for intra-molecular processes. Theory of molecular optical spectroscopy has been developed and widely utilized in studies of optical response of molecules either in the gas phase or chemisorbed on surfaces [1].

Recent progress in nano fabrication made it possible to perform optical experiments on molecular conduction junctions. In particular, current induced fluorescence[2] and Raman measurements[3–5] were reported in the literature. Theoretical description of optical response of such nonequilibrium open molecular systems is challenging due to necessity to account for optical excitations in the system in the presence of electron flux through the junction. For example, correlation between Stokes signal and conductance were measured[4] and an attempt of theoretical explanation of the effect was proposed[6, 7]. With scattering theory being inapplicable to the many-body electronic problem of quantum transport in junctions, the very definition of optical scattering processes in such systems is a challenge. Also, as discussed below, formal application of the molecular spectroscopy theory to junctions may be problematic.

Here we compare theoretical approaches utilized in the literature for description of optical spectroscopy of current carrying molecular junction. After introducing model of the junction subjected to external radiation field in Section II, we consider theoretical foundations of molecular spectroscopy in Section III. We then discuss Hilbert vs. Liouville space formulations in Section IV and quasiparticles vs. many-body states versions of the two formulations in Section V. In Section VI we specifically focus on different contributions to the total optical signal, and identify those relevant for the Raman scattering. Our conclusions are presented in Section VII.

## II. MODEL

We consider a junction formed by a molecule  $M$  coupled to two contacts  $L$  and  $R$  (each at its own thermal equilibrium) subjected to an external radiation field. Hamiltonian of the

model is

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (1)$$

$$\hat{H}_0 = \hat{H}_S + \sum_{B=L,R} \left( \hat{H}_B + \hat{V}_{SB} \right) + \hat{H}_{rad} \quad (2)$$

$$\hat{V} = \sum_{M,\alpha} \left( U_{M,\alpha} \hat{O}_M^\dagger \hat{a}_\alpha + H.c. \right) \quad (3)$$

where  $\hat{H}_0$  describes molecular junction and radiation field, and  $\hat{V}$  introduces coupling between them. Here  $\hat{H}_S$ ,  $\hat{H}_B$ , and  $\hat{H}_{rad}$  are Hamiltonians of the molecule (system), contacts (baths), and radiation field, respectively.  $\hat{H}_S$  describes electronic and vibrational structure of the molecule as well as arbitrary intra-molecular interactions. The contacts and field are assumed to be reservoirs of free electrons and photons, respectively

$$\hat{H}_B = \sum_{k \in B} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k \quad (4)$$

$$\hat{H}_{rad} = \sum_{\alpha} \nu_{\alpha} \hat{a}_{\alpha}^\dagger \hat{a}_{\alpha} \quad (5)$$

$\hat{V}_{SB}$  couples molecule with contacts and usually is assumed to be quadratic in the quasiparticle representation

$$\hat{V}_{SB} = \sum_{m \in S, k \in B} \left( V_{km} \hat{c}_k^\dagger \hat{d}_m + V_{mk} \hat{d}_m^\dagger \hat{c}_k \right) \quad (6)$$

In Eqs. (1)-(6)  $\hat{d}_m^\dagger$  ( $\hat{d}_m$ ) and  $\hat{c}_k^\dagger$  ( $\hat{c}_k$ ) are the creation (annihilation) operators of electron in level  $m$  of the molecule and state  $k$  of the contact, respectively.  $\hat{a}_\alpha^\dagger$  ( $\hat{a}_\alpha$ ) creates (destroys) photon in mode  $\alpha$  of the radiation field,  $\hat{O}_M^\dagger$  ( $\hat{O}_M$ ) is operator creating (destroying) molecular optical excitation  $M$ , and  $U_{M,\alpha}$  is coupling between the excitation  $M$  and mode  $\alpha$  of the radiation field. Here and below  $\hbar = e = 1$ .

### III. OPTICAL SIGNAL AS PHOTON FLUX

Similar to considerations of electron transport in junctions, theories of optical spectroscopy are mostly focused on simulating fluxes. More advanced treatments involve also higher cumulants of the counting statistics [8]. Diagrams for photon (boson) fluxes are presented in Fig. 1. As usual flux is defined as rate of population change in the continuum of modes  $\{\alpha\}$  of the radiation field, and corresponding expression for the photon flux from the

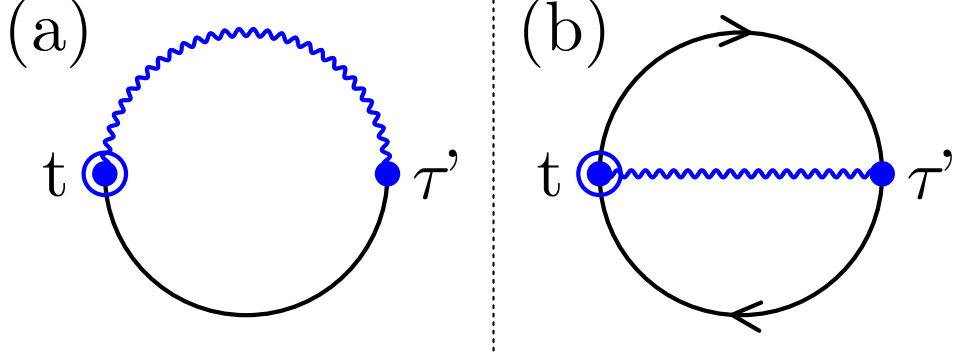


FIG. 1: Photon flux diagrams in (a) quasiparticle and (b) many-body states representations. Solid and wavy lines represent electron and photon propagators, respectively. Non-directed lines indicate both possible directions.  $t$  is the time of the flux,  $\tau'$  is the Keldysh contour integration variable. Summation over all indices and integration over contour variables is assumed for every connection in the diagrams (except the fixed time of the flux  $t$ ).

system into modes of the field at time  $t$  is [9, 10]

$$J(t) \equiv \sum_{\alpha} \frac{d}{dt} \langle \hat{a}_{\alpha}^{\dagger}(t) \hat{a}_{\alpha}(t) \rangle \quad (7)$$

$$= 2\text{Re} \int_{-\infty}^t dt' \text{Tr} \left[ \mathcal{G}^{>}(t, t') \Pi^{<}(t', t) - \mathcal{G}^{<}(t, t') \Pi^{>}(t', t) \right]$$

Here  $\text{Tr}[\dots]$  is trace over molecular optical excitations  $M$  (depending on the formulation these are either of quasiparticle type or represent transitions between many-body states of the molecule),  $\Pi^{<(>)}$  and  $\mathcal{G}^{<(>)}$  are lesser (greater) projections of the self-energy due to coupling to the radiation field and correlation (Green) function of molecular optical excitations, respectively [11]

$$\Pi_{M_1, M_2}(\tau', \tau) \equiv \sum_{\alpha} U_{M_1, \alpha} F_{\alpha}(\tau', \tau) U_{\alpha, M_2} \quad (8)$$

$$\mathcal{G}_{M_1, M_2}(\tau, \tau') \equiv -i \langle T_c \hat{O}_{M_1}(\tau) \hat{O}_{M_2}^{\dagger}(\tau') \rangle \quad (9)$$

where  $\tau$  and  $\tau'$  are the Keldysh contour variables corresponding to real times  $t$  and  $t'$ ,  $T_c$  is the contour ordering operator, and

$$F_{\alpha}(\tau', \tau) \equiv -i \langle T_c \hat{a}_{\alpha}(\tau') \hat{a}_{\alpha}^{\dagger}(\tau) \rangle \quad (10)$$

is the Green function of free photon evolution. Its lesser and greater projections are

$$F_{\alpha}^{<}(t', t) = -iN_{\alpha}e^{-i\nu_{\alpha}(t'-t)} \quad (11)$$

$$F_{\alpha}^{>}(t', t) = -i[1 + N_{\alpha}]e^{-i\nu_{\alpha}(t'-t)} \quad (12)$$

where  $N_{\alpha}$  is average population of the mode  $\alpha$ .

We note that expression (7) is exact. It consists of two contributions: in-scattering (photon absorbed by the system; first term in the second row) and out-scattering (photon emitted by the system; second term in the second row). The former characterizes e.g. absorption spectrum, while the latter can give information on fluorescence. Standard treatment proceeds by evaluating the molecular correlation functions  $\mathcal{G}^{(< >)}$  in the presence of intra-molecular interactions, coupling to environment (e.g. molecular coupling to contacts in junctions), and radiation field. Depending on the formulation some or all of these processes are taken into account in the molecular Green function through corresponding self-energies  $\Sigma$ . The latter usually can be evaluated only approximately. Corresponding expressions should be derived from the Luttinger-Ward functional [12], so that the resulting approximation fulfils conservation laws [13, 14]. The molecular Green function can be evaluated utilizing the Dyson equation

$$\mathcal{G}(\tau, \tau') = \mathcal{G}_0(\tau, \tau') + \int_c d\tau_1 \int_c d\tau_2 \mathcal{G}_0(\tau, \tau_1) \Sigma(\tau_1, \tau_2) \mathcal{G}(\tau_2, \tau') \quad (13)$$

where  $\mathcal{G}_0$  is the Green function in the absence of interactions. In most cases Eq. (13) has to be solved self-consistently due to dependence of the self-energy  $\Sigma$  on the molecular Green function. Substituting the converged result into (7) yields information on the incoming, outgoing, or total optical flux.

In practice treatment of molecular correlation function is often done in a simplified manner directly employing perturbation theory (at least in coupling to the radiation field). While this way conserving character of the approximation cannot be guaranteed (e.g. lowest order in electron-photon interaction - the Born approximation - is known to be non-conserving and in some cases may be not fully adequate [15]), the simplification avoids necessity of self-consistent treatment, and allows direct classification of multi-photon processes in the system. For example, expanding the Green function  $\mathcal{G}$ , Eq. (9), in perturbation series up to the second order in interaction with the radiation field  $\hat{V}$ , Eq. (3), yields

$$\mathcal{G}(\tau, \tau') = \mathcal{G}_0(\tau, \tau') - \int_c d\tau_1 \int_c d\tau_2 \Pi(\tau_1, \tau_2) \langle T_c \hat{O}(\tau) \hat{O}^{\dagger}(\tau_1) \hat{O}(\tau_2) \hat{O}^{\dagger}(\tau') \rangle_0 \quad (14)$$

where subscript 0 indicates that corresponding averages are evaluated in the absence of the field (intra-molecular interactions and coupling to contacts are still present). Substituting first term in the right into (7) yields lowest (second) order contributions into absorption (in-scattering) and emission (out-scattering) spectrum. Substitution of the second term in the right provides information on all fourth order optical processes in the system.

Below we focus on the out-scattering photon flux, second term in the bottom row of Eq. (7), and discuss fourth order optical processes, second term in the right of Eq. (14), in the emission spectrum within the Hilbert and Liouville space formulations. Following the tradition we pick one of the modes (or set of modes at particular frequency) in the sum (8), substitute it in place of the self-energy in second term in the bottom row of Eq. (7), and assume the mode (which we call final,  $f$ ) to be empty. Similarly, in Eq. (14) we pick one of the modes (which we call initial,  $i$ ) from the sum and use it in place of the self-energy in the expression. This leads to

$$J_{i \rightarrow f}(t) = 2 \text{Re} \int_{-\infty}^t dt' \int_c d\tau_1 \int_c d\tau_2 \sum_{M, M', M_1, M_2} U_{M', f} U_{f, M} U_{M_1, i} U_{i, M_2} F_f^>(t' - t) F_i(\tau_1, \tau_2) \langle T_c \hat{O}_{M'}^\dagger(t') \hat{O}_M(t) \hat{O}_{M_1}^\dagger(\tau_1) \hat{O}_{M_2}(\tau_2) \rangle \quad (15)$$

We note in passing that separation of the self-energies  $\Pi$  into modes in principle can be avoided (see e.g. Refs. 16, 17).

#### IV. HILBERT VS. LIOUVILLE SPACE FORMULATION

Difference between Hilbert vs. Liouville space formulations stems from the way projections of contour variables are performed. The Hilbert space formulation utilizes the Keldysh contour, and thus transition from contour variables to real times (i.e. ordering positions of the times on the contour) requires to work with several types of projected correlation functions (depending on positions of the times on the contour). The Liouville space formulation works with the real time axis, ordering the times relative to each other on the axis, and thus necessitates introduction of Liouville superoperators, whose role - distinguish between action on different branches of the contour - is exactly the same as that of different correlation functions projections in the Hilbert space formulation. Naturally, both formulations yield the same result [18–23].

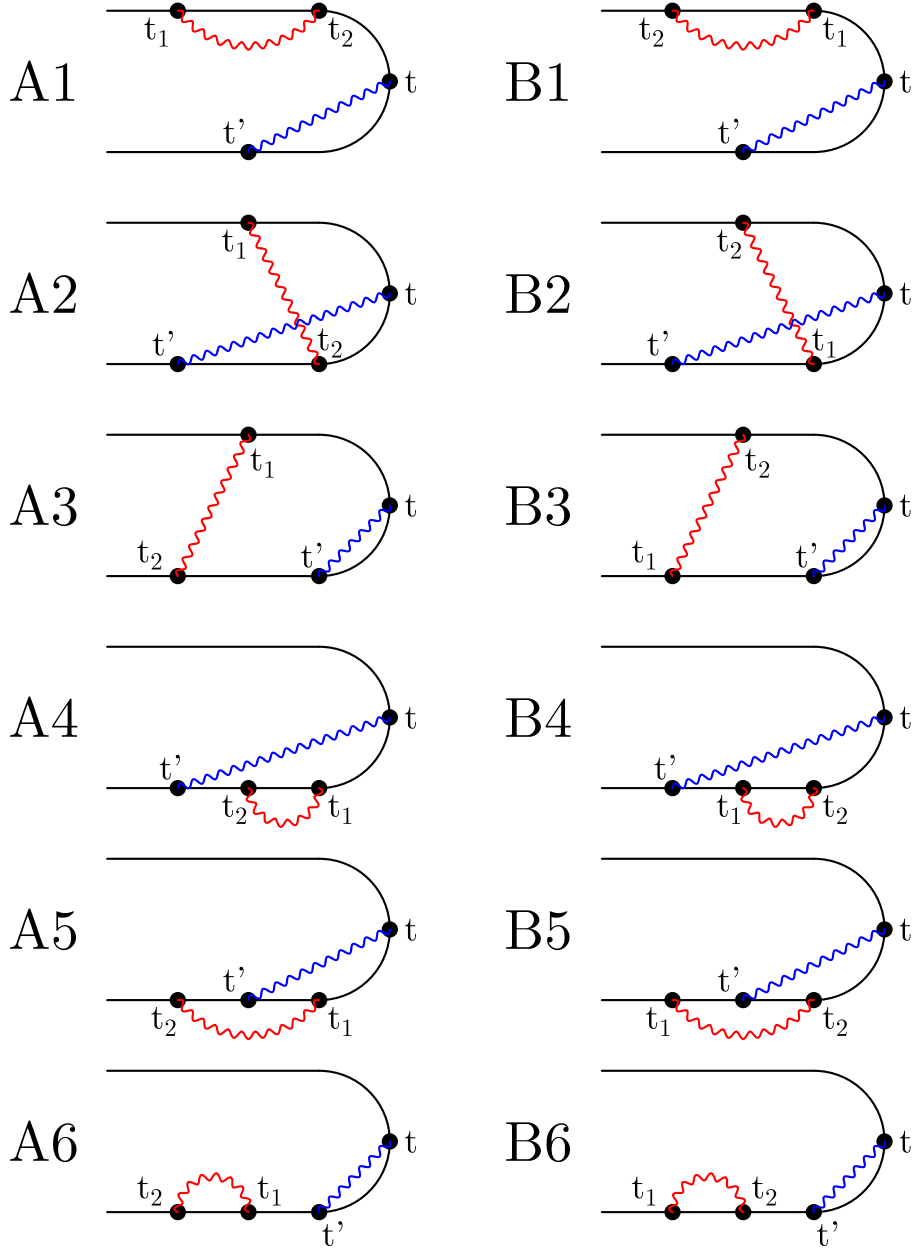


FIG. 2: Contour projections for the fourth order interaction with the modes  $i$  (red, times  $t_1$  and  $t_2$ ) and  $f$  (blue, times  $t$  and  $t'$ ) of the optical field. Time increases from left to right in these diagrams.

Utilizing the Hilbert space procedure in Eq. (15) is equivalent to consideration of all possible placements of times  $t_1$  and  $t_2$  (real times corresponding to contour variables  $\tau_1$  and  $\tau_2$ ) between times  $t$  and  $t'$  on the Keldysh contour. Note that in Eq. (15) the latter are placed in such a way that  $t'$  follows  $t$  on the contour (this results from the greater character of the

photon Green function  $F_f^>(t', t)$ ). These placements lead to 12 possible diagrams (i.e. time orderings on the contour) shown in Fig. 2. One can also get 12 additional diagrams, which are just complex conjugate versions of those presented in Fig. 2 (they come from the Re in Eq. (15)). Causal character of interactions implies that time  $t$  (the time of the signal) is the latest time, usually placed at the point where the two branches of the contour meet each other.  $t'$  then belongs to the anti-ordering branch, and  $t_1$  and  $t_2$  may populate any of the three regions (preceding  $t$ , between  $t$  and  $t'$  and after  $t'$  on the contour). Also times  $t$  and  $t'$  as well  $t_1$  and  $t_2$  are connected by lines representing free photon propagation described by Green functions  $F$ . Character of the Green functions (greater for the pair  $t$  and  $t'$ ,  $F_f^>(t', t)$ , and either greater or lesser for the pair  $t_1$  and  $t_2$ ,  $F_i^{>(<)}(t_1, t_2)$ ) depends on ordering of the times on the contour and represents photon emitted (for the greater projection, out-scattering) or absorbed (for the lesser projection, in-scattering) by the system.

The Liouville space procedure applied to Eq. (15) deals with the same problem of ordering variables  $\tau_1$  and  $\tau_2$  between the two times  $t$  and  $t'$ . However this time the ordering is performed along the real time axis (i.e. not only relative position of times on the contour but also relative position on the real time axis is tracked), thus number of diagrams (different orderings) is bigger here. Information on the branch of the contour is provided by the two-side Feynman diagrams (the Keldysh contour diagrams with additional restriction on the relative positions of times with respect to the real time axis). It is customary to indicate each photon process by separate arrow in these diagrams, rather than consider contractions representing free photon propagation. The agreement is that arrow pointing to the left corresponds to creation operator of the photon in quantum mechanical description of the field (or factor  $e^{i\nu t}$  for classical treatment of the field), while arrow pointing to the right represents operator of annihilation of the photon (or factor  $e^{-i\nu t}$ ) [1]. The procedure being applied to expression (15) leads to 24 double-sided Feynman diagrams presented in Fig. 3. These are the diagrams presented in Figs. 4 and 5 of Ref. 24. Similar to the Hilbert space formulation 24 more diagrams are complex conjugate variants.

Comparison of the two sets of diagrams is straightforward, when one keeps in mind an additional restriction on time ordering within the Liouville space formulation (ordering not only on the contour but also with respect to real time axis). So, one Hilbert space type diagram (see Fig. 2) may encompass several diagrams of the Liouville type (see Fig. 3). Diagram-to-diagram correspondence is shown in Fig. 4.



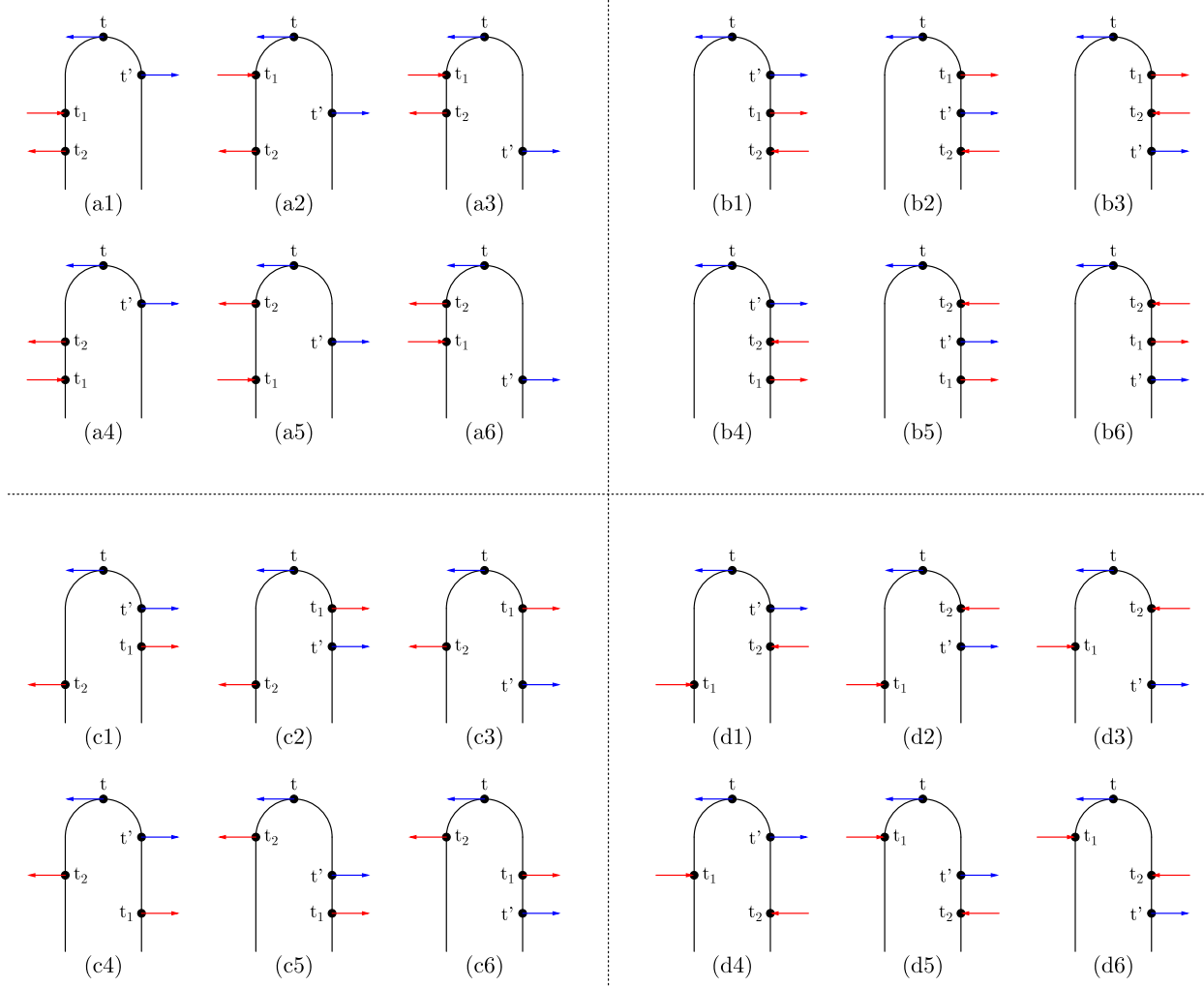


FIG. 3: Contour projections (double-sided Feynman diagrams) for the fourth order interaction with the modes  $i$  (red, times  $t_1$  and  $t_2$ ) and  $f$  (blue, times  $t$  and  $t'$ ) of the optical field. Time increases from bottom to top.

## V. QUASIPARTICLES VS. MANY-BODY STATES APPROACH

In realistic simulations in junctions in addition to molecular interaction with radiation field other intra-molecular interactions (e.g. electron-electron or electron-phonon) and couplings to environment (e.g. coupling to contacts) should be accounted for.

Quasiparticles approaches (in either Hilbert or Liouville space) are usually efficient in treating molecule-contacts couplings. Indeed, since the latter are represented as quadratic in terms of elementary excitations, Eq. (6), they do not alter non-interacting character of the Hamiltonian, and thus Wick's theorem is available to exactly evaluate multi-time correlation

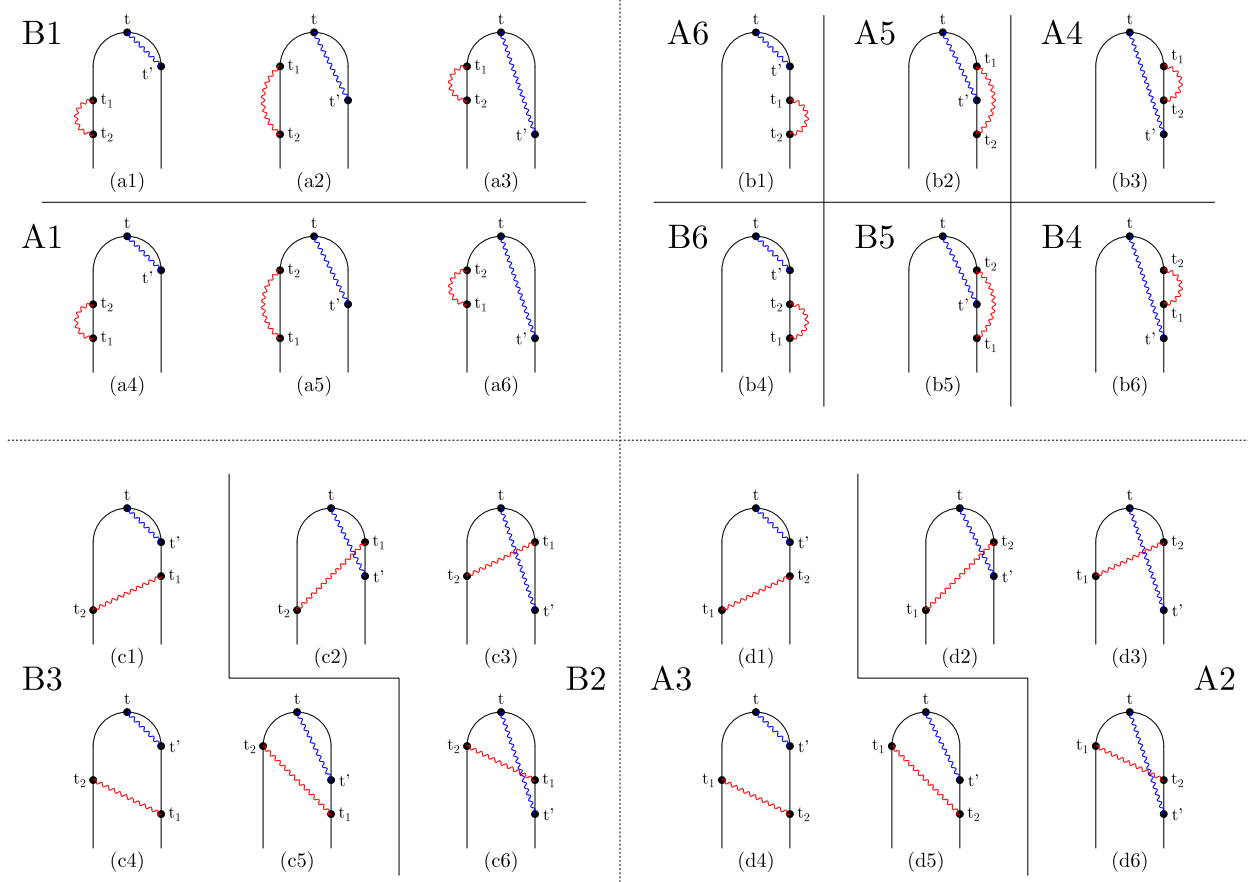


FIG. 4: Comparison between contour projections presented within the Hilbert (see Fig. 2) and Liouville (see Fig. 3) space approaches. Time increases from bottom to top.

functions in presence of the couplings [25]. However, quasiparticles are less convenient when dealing with intra-molecular interactions. That is, if intra-molecular interactions are weak compared to either molecule-contacts couplings or separation between electron energy from molecular resonances, standard diagrammatic technique (on the contour perturbation theory) can be invoked to account approximately for the interactions.

For strong interactions (e.g. Coulomb blockade or polaron formation) usually encountered in the resonant tunneling regime, a nonequilibrium atomic limit (i.e. consideration utilizing many-body states of the isolated molecule as a basis) is preferable [26]. Note that historically spectroscopy of isolated molecules also was formulated mostly in the language of many-body states (molecular or dressed states of molecule and the field) [1]. Many-body states based formulations, while accounting exactly for intra-molecular interactions, are capable of treating molecule-contacts couplings only approximately. We note that such approximate

schemes exist for both Hilbert [27–29] and Liouville [30–32] space formulations, however these approximations are not well controlled.

A promising tool is the Hilbert space type pseudoparticle NEGF (PP-NEGF) technique [33–36], which while being a many-body states formulation allows to take into account coupling to the contacts within well controllable diagrammatic technique, which is based on extension of the standard methods of quantum field theory into extended version of the Hilbert space. The PP-NEGF has several important advantages: 1. The method is conceptually simple; 2. Its practical implementations rely on a set of controlled approximations (standard diagrammatic perturbation theory techniques can be applied); 3. Already in its simplest implementation, the non-crossing approximation (NCA), the pseudoparticle NEGF goes beyond standard QME approaches by accounting for both non-Markovian effects and hybridization of molecular states; 4. The method is capable of treating junction problems in the language of many-body states of the isolated molecule, exactly accounting for all the on-the-molecule interactions. Recently a first application of the methodology to problems of optical spectroscopy of junctions was proposed in Ref. 37.

## VI. RAMAN SPECTROSCOPY

Eq. (15) represents all contributions to the fourth order optical process. Note that interaction with mode  $f$  only includes outgoing photon, while interactions with mode  $i$  have both incoming and outgoing photon contributions. Correspondingly, the projections can be separated into those containing two outgoing photons (diagrams B in Fig. 2) and those which contain incoming photon of mode  $i$  and outgoing photon of mode  $f$  (diagrams A in Fig. 2). The former contribute to fluorescence (both coherent fourth order and sequential second order processes), while the latter yield Raman (see below) and absorption with emission (sequential second order) processes.

Both diagrams A and B of Fig. 2 contain virtual photon processes. For example, interaction with mode  $i$  in projections (a4) (A type diagram) and (a1) (B type diagram) of Fig. 3 are virtual photon processes. These processes yield renormalization of molecular correlation functions due to presence of the radiation field. Accounting for such processes within the procedure described above should be done with care. Indeed, reasonable estimate of the interaction with the field is  $U \sim 10^{-3} - 10^{-2}$  eV [38]. For a molecule chemisorbed on metallic

surface electronic escape rate (characteristic strength of the molecule-contact interaction) is  $\Gamma \sim 0.01 - 0.1$  eV [39], and in this case renormalizations due to coupling to contacts are much more pronounced. For a molecule detached from contacts renormalizations due to the radiation field become important, however proper way to account for those is by solving Eq. (13). Accounting for the renormalization by keeping only second term in the right of Eq. (14) (besides being a non-conserving approximation) results in a Green function divergent at molecular resonances. Resummation of the perturbation series and introduction of the retarded projection of the self-energy is the proper way to account for the renormalization, when coupling to the radiation field is weak relative to intra-molecular interactions. If coupling to the radiation field is the dominating interaction, perturbation series treatment becomes invalid. We stress that in experiment one deals with the total optical signal, and a proper theoretical treatment should utilize Eq. (7) with conserving approximations employed to evaluate molecular Green functions.

We now focus on theoretical description of a particular optical process - the Raman scattering. Raman scattering from mode  $i$  to mode  $f$  is a coherent process of (at least) fourth order in coupling to radiation field with two orders in coupling to incoming photon of mode  $i$  and two orders in coupling to outgoing photon of mode  $f$ . The process should also satisfy a proper energy conservation: at steady-state difference between incoming and outgoing photon frequencies should be equal to multiples of the frequency of molecular vibration (may be plus electronic energy differences within the same electronic level or many-body state broadened by coupling to environment)

$$J_{i \rightarrow f}^{Raman} \sim \delta(\nu_i - \nu_f + n\omega_v + \Delta E) \quad (16)$$

Here  $n$  is integer number ( $n = 0$  yields Rayleigh scattering) and  $\Delta E$  is electronic energy change within the same broadened level or many-body state.

Identification of diagramms related to Raman scattering requires some care. An easy way to identify relevant contributions relies on the Hilbert space formulation of section IV with utilization of the Langreth projection rules [11]. First, only projections A of Fig. 2 are those corresponding to a process with one incoming and one outgoing photon. Second, among those only parts of projections A2, A3, A4, and A5 yield proper energy conservation, Eq. (16). For example, let employ the Langreth rules to projection A4. This yields 4 terms

in expression (15)

$$\int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t) \int_{-\infty}^0 d(t_2 - t_1) \dots \quad (17a)$$

$$- \int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t) \int_{-\infty}^0 d(t_2 - t') \dots \quad (17b)$$

$$- \int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t') \int_{-\infty}^0 d(t_2 - t_1) \dots \quad (17c)$$

$$+ \int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t') \int_{-\infty}^0 d(t_2 - t') \dots \quad (17d)$$

Only (17b) yields proper energy conservation. Similarly, application of the Langreth rules to projection A3 yields one, and to projections A2 and A5 yields two integrals for each with only one term in each case satisfying restrictions of the Raman process.

In Refs. 10, 40 we presented a theory of Raman scattering in molecular junctions formulated within the NEGF (the Hilbert space quasiparticle formulation). Projections presented there were different from those given in Fig. 2 in two aspects: a. the projections there are given after the Langreth rules have been applied and b. some of the projections (see e.g. Fig. 8b of Ref. 10) represent ‘the hole view’ of scattering process. We note that in general (when explicit time-dependent processes or a magnetic field are present) the latter flexibility does not exist. However for steady-state situation the two pictures can be shown to be equivalent. For example, the contribution (17b) to the Raman signal is (note, it is easy to see that the contribution is real following the derivation leading from Eq.(28) to Eq.(56) in Ref. 10)

$$\begin{aligned} & |U_i U_f|^2 N_i \int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t) \int_{-\infty}^0 d(t_2 - t') e^{i\nu_f(t-t') - i\nu_i(t_1-t_2)} \\ & \quad \times \langle \hat{O}^\dagger(t') \hat{O}(t_2) \hat{O}^\dagger(t_1) \hat{O}(t) \rangle \\ & \equiv |U_i U_f|^2 N_i \int_{-\infty}^{+\infty} d(t' - t) \int_{-\infty}^0 d(t_1 - t) \int_{-\infty}^0 d(t_2 - t') e^{-i\nu_f(t-t')} e^{i\nu_i(t_1-t_2)} \\ & \quad \times \langle \hat{O}^\dagger(t) \hat{O}(t_1) \hat{O}^\dagger(t_2) \hat{O}(t') \rangle \end{aligned}$$

where  $N_i$  is the population of the mode  $i$ . Then utilizing the time-reversal symmetry of the molecular correlation function,[41]

$$\langle \hat{O}^\dagger(t) \hat{O}(t_1) \hat{O}^\dagger(t_2) \hat{O}(t') \rangle = \langle \hat{O}^\dagger(-t') \hat{O}(-t_2) \hat{O}^\dagger(-t_1) \hat{O}(-t) \rangle \quad (18)$$

and inverting signs of the time variables one gets Eq. (29) of Ref. 10, which was derived from ‘the hole type’ projection shown in Fig. 8b there. We note that while the results are

equivalent, graphical forms of the projections differ: Fig. 8b of Ref. 10 has the two incoming field modes on different branches, while the diagram A4 - on the same branch.

## VII. CONCLUSION

We discussed theoretical formulations utilized in studies of optical processes in current carrying molecular junctions. We start by identifying total optical signal as photon flux from the system to registering device, for which exact formulation in terms of molecular correlation (Green) functions is available. Standard quantum field theory methods allow to formulate well controlled conserving approximation to evaluate the Green functions of the molecule. At the same time tradition coming from the theory of optical spectroscopy for isolated molecules utilizes perturbation theory. The latter, while not being a conserving approximation, allows to separate different photon scattering events in the total optical signal. We discussed the Hilbert and Liouville space formulations, indicating similarities and differences in graphical representations of photon scattering process in the two formulations. We also pointed out strong and weak sides of quasiparticles (second quantization) vs. many-body states based (nonequilibrium atomic limit) approaches in both formulations, and outlined the PP-NEGF as a promising theoretical approach to study optical spectroscopy in junctions. Finally, we focused on theoretical formulation for Raman scattering in molecular junctions, and clarified questions raised in the literature [24] with respect to identification of relevant projections and obtaining corresponding contributions to the total optical signal. Thus, the paper bridges different formulations of optical spectroscopy in open nonequilibrium systems.

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- [1] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Vol. 6 (Oxford University Press, 1995).
  - [2] S. W. Wu, G. V. Nazin, and W. Ho, “Intramolecular photon emission from a single molecule in a scanning tunneling microscope,” *Phys. Rev. B* **77**, 205430 (2008).
  - [3] Z. Ioffe, T. Shamai, A. Ophir, G. Noy, I. Yutsis, K. Kfir, O. Cheshnovsky, and Y. Selzer, “Detection of heating in current-carrying molecular junctions by raman scattering,” *Nature Nanotechnology* **3**, 727–732 (2008).

- [4] D. R. Ward, N. J. Halas, J. W. Ciszek, J. M. Tour, Y. Wu, P. Nordlander, and D. Natelson, “Simultaneous measurements of electronic conduction and raman response in molecular junctions,” *Nano Lett.* **8**, 919–924 (2008).
- [5] D. R. Ward, D. A. Corley, J. M. Tour, and D. Natelson, “Vibrational and electronic heating in nanoscale junctions,” *Nature Nanotechnology* **6**, 33–38 (2011).
- [6] T.-H. Park and M. Galperin, “Correlation between raman scattering and conductance in a molecular junction,” *EPL* **95**, 27001 (2011).
- [7] T.-H. Park and M. Galperin, “Charge transfer contribution to surface-enhanced raman scattering in a molecular junction: Time-dependent correlations,” *Phys. Rev. B* **84**, 075447 (2011).
- [8] M. Esposito, U. Harbola, and S. Mukamel, “Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems,” *Rev. Mod. Phys.* **81**, 1665–1702 (2009).
- [9] M. Galperin, A. Nitzan, and M. A. Ratner, “Heat conduction in molecular transport junctions,” *Phys. Rev. B* **75**, 155312 (2007).
- [10] M. Galperin, M. A. Ratner, and A. Nitzan, “Raman scattering in current-carrying molecular junctions,” *J. Chem. Phys.* **130**, 144109 (2009).
- [11] H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer, Berlin Heidelberg, 2008).
- [12] J. M. Luttinger and J. C. Ward, “Ground-state energy of a many-fermion system. ii,” *Phys. Rev.* **118**, 1417–1427 (1960).
- [13] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics*, Frontiers in Physics (W. A. Benjamin, Inc., New York, 1962).
- [14] P. Myöhänen, A. Stan, G. Stefanucci, and R. van Leeuwen, “Kadanoff-baym approach to quantum transport through interacting nanoscale systems: From the transient to the steady-state regime,” *Phys. Rev. B* **80**, 115107 (2009).
- [15] T.-H. Park and M. Galperin, “Self-consistent full counting statistics of inelastic transport,” *Phys. Rev. B* **84**, 205450 (2011).
- [16] A. J. White, B. D. Fainberg, and M. Galperin, “Collective plasmon-molecule excitations in nanojunctions: Quantum consideration,” *J. Phys. Chem. Lett.* **3**, 2738–2743 (2012).
- [17] A. Baratz, A. J. White, M. Galperin, and R. Baer, “The effects of electromagnetic coupling on conductance switching of a gated tunnel junction,” *J. Phys. Chem. Lett.* **5**, 3545–3550 (2014).

- [18] J. Schwinger, “Brownian motion of a quantum oscillator,” *J. Math. Phys.* **2**, 407–432 (1961).
- [19] L. V. Keldysh, “Diagram technique for nonequilibrium processes,” *Sov. Phys. JETP* **20**, 1018–1026 (1965).
- [20] R. A. Craig, “Perturbation expansion for real-time green’s functions,” *J. Math. Phys.* **9**, 605–611 (1968).
- [21] H. Schoeller and G. Schön, “Mesoscopic quantum transport: Resonant tunneling in the presence of a strong coulomb interaction,” *Phys. Rev. B* **50**, 18436–18452 (1994).
- [22] U. Harbola and S. Mukamel, “Nonequilibrium superoperator GW equations,” *J. Chem. Phys.* **124**, 044106 (2006).
- [23] U. Harbola and S. Mukamel, “Superoperator nonequilibrium green’s function theory of many-body systems; applications to charge transfer and transport in open junctions,” *Physics Reports* **465**, 191 – 222 (2008).
- [24] U. Harbola, B. K. Agarwalla, and S. Mukamel, “Frequency-domain stimulated and spontaneous light emission signals at molecular junctions,” *J. Chem. Phys.* **141**, 074107 (2014).
- [25] P. Danielewicz, “Quantum theory of nonequilibrium processes, i,” *Ann. Phys.* **152**, 239–304 (1984).
- [26] A. J. White, M. A. Ochoa, and M. Galperin, “Nonequilibrium atomic limit for transport and optical response of molecular junctions,” *J. Phys. Chem. C* **118**, 11159–11173 (2014).
- [27] I. Sandalov, B. Johansson, and O. Eriksson, “Theory of strongly correlated electron systems: Hubbard-anderson models from an exact hamiltonian, and perturbation theory near the atomic limit within a nonorthogonal basis set,” *Int. J. Quant. Chem.* **94**, 113–143 (2003).
- [28] J. Fransson, “Nonequilibrium theory for a quantum dot with arbitrary on-site correlation strength coupled to leads,” *Phys. Rev. B* **72**, 075314 (2005).
- [29] M. Galperin, A. Nitzan, and M. A. Ratner, “Inelastic transport in the coulomb blockade regime within a nonequilibrium atomic limit,” *Phys. Rev. B* **78**, 125320 (2008).
- [30] M. Leijnse and M. R. Wegewijs, “Kinetic equations for transport through single-molecule transistors,” *Phys. Rev. B* **78**, 235424 (2008).
- [31] M. Esposito and M. Galperin, “Transport in molecular states language: Generalized quantum master equation approach,” *Phys. Rev. B* **79**, 205303 (2009).
- [32] R. B. Saptsov and M. R. Wegewijs, “Fermionic superoperators for zero-temperature nonlinear transport: Real-time perturbation theory and renormalization group for anderson quantum



- dots,” Phys. Rev. B **86**, 235432 (2012).
- [33] N. Tsuji and P. Werner, “Nonequilibrium dynamical mean-field theory based on weak-coupling perturbation expansions: Application to dynamical symmetry breaking in the hubbard model,” Phys. Rev. B **88**, 165115 (2013).
  - [34] J. H. Oh, D. Ahn, and V. Bubanja, “Transport theory of coupled quantum dots based on the auxiliary-operator method,” Phys. Rev. B **83**, 205302 (2011).
  - [35] A. J. White and M. Galperin, “Inelastic transport: a pseudoparticle approach,” Phys. Chem. Chem. Phys. **14**, 13809–13819 (2012).
  - [36] H. Aoki, N. Tsuji, M. Eckstein, M. Kollar, T. Oka, and P. Werner, “Nonequilibrium dynamical mean-field theory and its applications,” Rev. Mod. Phys. **86**, 779–837 (2014).
  - [37] A. J. White, S. Tretiak, and M. Galperin, “Raman scattering in molecular junctions: A pseudoparticle formulation,” Nano Letters **14**, 699–703 (2014).
  - [38] M. Sukharev and M. Galperin, “Transport and optical response of molecular junctions driven by surface plasmon polaritons,” Phys. Rev. B **81**, 165307 (2010).
  - [39] I. Kinoshita, A. Misu, and T. Munakata, “Electronic excited state of NO adsorbed on Cu(111): A two-photon photoemission study,” J. Chem. Phys. **102**, 2970–2976 (1995).
  - [40] M. Galperin, M. A. Ratner, and A. Nitzan, “Raman scattering from nonequilibrium molecular conduction junctions,” Nano Lett. **9**, 758–762 (2009).
  - [41] L. A. Bányai, *Lectures on Non-Equilibrium Theory of Condensed Matter* (World Scientific, 2006).